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EFFECT OF SODIUM CHLORIDE ON THE pH OF *p*-PHENOL-SULFONATE BUFFERS FROM 0° TO 60° C

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ABSTRACT

The electromotive forces developed between the hydrogen and silver chloride electrodes of galvanic cells which contained 12 mixtures of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride were measured from 0° to 60° C at intervals of 5 degrees. Sufficient alkali was used to neutralize half of the phenolsulfonate in each solution. The molal ratios of sodium hydroxide to sodium chloride were 10, 4, 2, and 1. The pH of each solution, and of six phenolsulfonate buffers without sodium chloride, was determined. Equations are given to represent the change of pH at each of the 13 temperatures with molality of sodium chloride. It is shown that the ionic strength and pH of unknowns may be obtained approximately, and the usual salt errors largely eliminated, from emf measurements on two portions of the unknown solution to which different amounts of sodium chloride have been added.

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I. INTRODUCTION

Buffers composed of potassium *p*-phenolsulfonate and sodium hydroxide are satisfactory for the control of alkalinity and for the calibration of pH equipment in the slightly alkaline region between pH 8.5 and pH 9.0 [1].¹ Potassium phenolsulfonate is easily purified, is anhydrous and nonhygroscopic [2], and its aqueous solutions are stable from 0° to 60° C when reasonable protection from strong light is provided.

Cells with hydrogen and silver chloride electrodes were used in the determination of the second dissociation constant of *p*-phenolsulfonic acid and the pH values of phenolsulfonate-chloride mixtures [1]. The cells contained known concentrations both of the buffer salts and of sodium chloride.

¹ Figures in brackets indicate the literature references at the end of this paper.

In the list of provisional pH standards given in an earlier publication [3], the pH values of buffers containing chloride were reported. These buffer solutions can therefore be used in hydrogen-silver-chloride cells without liquid junction, as well as in cells which involve a liquid junction and calomel electrode. In most practical work, however, sodium chloride serves no useful purpose in a standard buffer solution apart from its small influence on the pH value and from the usually negligible increase in precision of the emf measurement which results from the increased conductance of the mixture. The effect of the salt upon the buffer capacity, stability, and other desirable properties of the solution is so small as to be without significance. If the influence of the sodium chloride upon the activity coefficients and pH values of the buffers were known, the inconvenience of adding chloride to buffers prepared as calibration standards could be avoided.

The effect of neutral salts upon the behavior of buffer solutions is of further interest in its bearing on the spectral properties of mixtures which contain tautomeric ions in homogeneous equilibrium. It has been shown [2] that phenolsulfonate buffers have characteristic absorption bands in the ultraviolet region of the spectrum similar to those of indicator ions and molecules in the visible region. Furthermore, studies of the effect of salts on the absorptive properties of indicator ions and molecules suggest that the activity coefficients of these tautomeric ions change normally with increase of ionic strength up to about 0.5, but specific salt effects larger than the experimental errors are observed if the indicator is dissolved in solutions which are 0.5 to 2 *M* with respect to various salts [4, 5].

This paper reports a study of 12 equimolal mixtures of potassium *p*-phenolsulfonate and potassium sodium *p*-phenolate sulfonate with 4 different molal ratios of sodium chloride to buffer salt at 5-degree intervals from 0° to 60° C. Electromotive-force measurements were made at the 13 temperatures, and the pH values were calculated. The influence of sodium chloride on the pH was shown to be a "normal salt effect." Equations were formulated to express the observed change of pH with molality of sodium chloride, and the calculated pH values of *p*-phenolsulfonate buffers without sodium chloride are given. Estimation of the ionic strength of a mixture of potassium *p*-phenolsulfonate and sodium hydroxide from the change in emf which results on the addition of sodium chloride to the buffer and application of the method to unknowns are discussed.

II. EXPERIMENTAL PROCEDURE AND THE CALCULATION OF pH

The purification and analysis of potassium *p*-phenolsulfonate and sodium chloride, the preparation and standardization of a carbonate-free solution of sodium hydroxide, the preparation of the buffer solutions from these materials and conductivity water in an atmosphere freed of carbon dioxide, and other details of the experimental technique have been described [1, 6].

The emf values given in table 1 have been corrected in the usual way to a partial pressure of hydrogen of 760 mm. The four solutions ²

² The buffers of series A are, respectively, solutions A1, A2, A4, and A6 prepared in the earlier study of phenolsulfonate-chloride mixtures [1]. As before, HPs will be written for the univalent phenolsulfonate anion, $\text{HOCC}_6\text{H}_4\text{SO}_3^-$, and Ps for the bivalent phenolate-sulfonate anion, $\text{OCC}_6\text{H}_4\text{SO}_3^{2-}$.

of series A contain approximately the same molal concentration of sodium chloride, m_3 , as of potassium *p*-phenolsulfonate (KHPs), m_1 , and of potassium sodium *p*-phenolatesulfonate (KNaPs), m_2 , whereas series B, C, and D comprise solutions which have, respectively, one-half, one-quarter, and one-tenth as much sodium chloride as buffer salt. The molalities of each constituent are given in columns 2, 3, and 4 of table 1.

TABLE 1.—*Electromotive forces of hydrogen-silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3)*

Solution number	m_1	m_2	m_3	E_0°	E_5°	E_{10}°	E_{15}°	E_{20}°
A1.....	0.09628	0.09744	0.09622	0.78744	0.79105	0.79460	0.79807	0.80156
A2.....	.05979	.06051	.05975	.79000	.80295	.80674	.81048	.81418
A3.....	.03070	.03107	.03068	.81578	.82003	.82419	.82830	.83235
A4.....	.006425	.009539	.009419	.84605	.85091	.85570	.86040	.86502
B1.....	.10376	.09751	.04951	.80171	.80555	.80928	.81302	.81672
B2.....	.04853	.04561	.02316	.82037	.82464	.82883	.83294	.83705
B3.....	.017932	.016851	.008556	.84581	.85057	.85521	.85989	.86451
C1.....	.09736	.09753	.02549	.81894	.82308	.82714	.83117	.83520
C2.....	.04058	.04065	.010626	.84046	.84513	.84969	.85417	.85868
D1.....	.09736	.09753	.010051	.84090	.84545	.84991	.85434	.85876
D2.....	.04594	.04682	.004743	.85945	.86440	.86929	.87410	.87893
D3.....	.019838	.019872	.002048	.88062	.88601	.89130	.89658	.90190
	E_{25}°	E_{30}°	E_{35}°	E_{40}°	E_{45}°	E_{50}°	E_{55}°	E_{60}°
A1.....	0.80500	0.80839	0.81169	0.81506	0.81833	0.82159	0.82482	0.82808
A2.....	.81793	.82157	.82517	.82878	.83229	.83583	.83930	.84278
A3.....	.83644	.84046	.84441	.84839	.85224	.85613	.85993	.86376
A4.....	.86979	.87434	.87888	.88343	.88789	.89234	.89664	.90104
B1.....	.82042	.82404	.82764	.83120	.83475	.83827	.84175	.84524
B2.....	.84116	.84525	.84916	.85317	.85708	.86097	.86485	.86874
B3.....	.86923	.87385	.87824	.88278	.88717	.89164	.89599	.90015
C1.....	.83926	.84323	.84709	.85102	.85489	.85875	.86255	.86636
C2.....	.86321	.86770	.87200	.87642	.88074	.88507	.88935	.89361
D1.....	.86322	.86761	.87179	.87611	.88040	.88462	.88885	.89303
D2.....	.88376	.88858	.89319	.89789	.90259	.90721	.91175	.91626
D3.....	.90730	.91251	.91748	.92233	.92770	.93262	.93752	.94228

The pH values of the mixtures of *p*-phenolsulfonate, *p*-phenolate sulfonate, and chloride salts can be computed readily from the equation³

$$\text{pH} = (E - E^\circ)/k + \log m_{\text{Cl}} - A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}) + \beta\mu, \quad (1)$$

provided that the parameters a_i and β have been determined. It is possible to find the necessary values of a_i from the change of the next to the last term of eq 1 with ionic strength. This change is observed most simply by plotting $\text{p}K'_2$, the negative of the common logarithm of the "apparent" second dissociation constant of phenolsulfonic acid, as a function of ionic strength, where $\text{p}K'_2$ is given by

$$\text{p}K'_2 = (E - E^\circ)/k + \log (m_{\text{HPs}}m_{\text{Cl}}/m_{\text{Ps}}) + 2A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}). \quad (2)$$

³ E and E° represent the emf and standard potential of the cell which contains hydrogen and silver chloride electrodes, and k is $2.3026RT/F$. A and B are constants of the Debye-Hückel equation. A recalculation of A , B , and k was recently reported [7]. No change was made in the value of k between 0° and 60° C, and E° therefore remains unaltered. A new extrapolation curve computed from the emf data of Harned and Ehlers [8] (from which E° is derived) would, however, show a slightly different slope, as a result of the small changes that were made in the values of A and B .

The ionic strength, μ , is given by $m_1 + 3m_2 + m_3 - m_{\text{OH}}$. The calculation of m_{OH} from the dissociation constants of water and of the phenol group was made as described in the earlier paper [1].

The proper value of a_1 gives a straight-line plot of pK'_2 with respect to ionic strength. This straight line extrapolates to pK_2 , the negative of the common logarithm of the thermodynamic dissociation constant, at an ionic strength of zero. Since pK'_2 and pK_2 are then both known, β is readily obtained from the equation

$$\beta = (pK_2 - pK'_2)/\mu. \quad (3)$$

A value of 8.0 Å for a_1 was found to yield pK'_2 values that varied linearly with ionic strength for each series of solutions at all 13 temperatures. Extrapolation of these lines to zero ionic strength yielded, within the error of the experiments, the same values of pK_2 as were obtained in the detailed study of 39 solutions with 2 different buffer ratios [1].

The plots of pK'_2 as a function of ionic strength for the four series of buffers at 0°, 25°, and 60° C are shown in figure 1. A correction for hydrolysis was made [1]. The values of $3A$, $8B$, and β are listed in table 2.

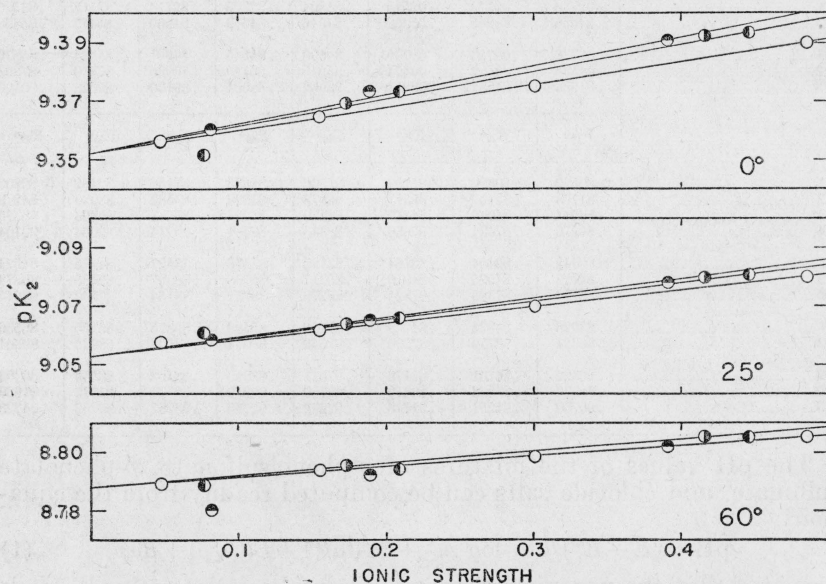


FIGURE 1.—Plot of pK'_2 (eq 2) as a function of ionic strength at 0°, 25°, and 60° C.

○—series A; ●—series B; ◐—series C; ◑—series D

TABLE 2.—Numerical values of βA , βB , and β from 0° to 60° C

t $^\circ\text{C}$	βA	βB	$-\beta$ for series		
			A	B	C and D
0	1.467	2.602	0.079	0.094	0.100
5	1.478	2.609	.075	.087	.092
10	1.490	2.616	.069	.077	.082
15	1.503	2.623	.066	.074	.078
20	1.516	2.631	.061	.069	.071
25	1.529	2.638	.057	.063	.066
30	1.544	2.647	.052	.057	.061
35	1.559	2.656	.049	.053	.053
40	1.575	2.664	.046	.051	.051
45	1.591	2.674	.042	.047	.047
50	1.607	2.682	.040	.045	.045
55	1.625	2.693	.040	.045	.045
60	1.643	2.702	.038	.043	.043

The pH of each mixture is given in table 3. These values were computed from eq 1 with the use of 8.0 A for a_i and the values of β given in table 2. The error in establishing a_i is estimated to be about ± 0.2 A, and the uncertainty in pH from this source is somewhat less than 0.002 unit.

TABLE 3.—pH values of mixtures of potassium *p*-phenolsulfonate (m_1), potassium sodium *p*-phenolate sulfonate (m_2), and sodium chloride (m_3)

Solution number	m_1	m_2	m_3	pH at—				
				0°	5°	10°	15°	20°
A1.....	0.09628	0.09744	0.09622	8.992	8.923	8.857	8.795	8.738
A2.....	.05979	.06051	.05975	9.024	8.956	8.889	8.828	8.770
A3.....	.03070	.03107	.03068	9.072	9.003	8.937	8.876	8.818
A4.....	.009425	.009539	.009419	9.154	9.085	9.025	8.959	8.901
B1.....	.10376	.09751	.04951	8.967	8.897	8.831	8.769	8.711
B2.....	.04853	.04561	.02316	9.022	8.951	8.885	8.823	8.765
B3.....	.017932	.016851	.008556	9.093	9.023	8.955	8.890	8.837
C1.....	.09736	.09753	.02549	8.998	8.928	8.862	8.800	8.743
C2.....	.04058	.04065	.010626	9.059	8.990	8.924	8.861	8.805
D1.....	.09736	.09753	.010051	9.004	8.933	8.867	8.805	8.747
D2.....	.04594	.04682	.04743	9.056	8.986	8.920	8.856	8.800
D3.....	.019838	.019872	.002048	9.113	9.042	8.976	8.914	8.857
	pH at—							
	25°	30°	35°	40°	45°	50°	55°	60°
A1.....	8.682	8.633	8.585	8.542	8.502	8.464	8.427	8.395
A2.....	8.715	8.665	8.618	8.575	8.535	8.498	8.461	8.429
A3.....	8.763	8.713	8.667	8.624	8.584	8.547	8.511	8.479
A4.....	8.848	8.797	8.751	8.709	8.669	8.632	8.595	8.564
B1.....	8.656	8.606	8.559	8.514	8.475	8.437	8.400	8.368
B2.....	8.709	8.660	8.612	8.568	8.527	8.490	8.454	8.422
B3.....	8.783	8.735	8.686	8.643	8.601	8.567	8.531	8.495
C1.....	8.689	8.638	8.591	8.547	8.509	8.470	8.433	8.401
C2.....	8.750	8.700	8.653	8.609	8.570	8.533	8.498	8.466
D1.....	8.692	8.642	8.594	8.550	8.511	8.472	8.436	8.404
D2.....	8.744	8.694	8.647	8.602	8.564	8.527	8.490	8.456
D3.....	8.804	8.754	8.706	8.658	8.621	8.582	8.546	8.510

III. EQUATIONS FOR THE SALT EFFECT

The negative of the logarithm of the mean activity coefficient of hydrochloric acid ($f_{\pm} = \sqrt{f_H f_{Cl}}$) in each series of *p*-phenolsulfonate-chloride mixtures is expressed by

$$-\log f_{\pm} = \frac{A\sqrt{\mu}}{1 + 8B\sqrt{\mu}} - \beta\mu, \quad (4)$$

where f represents the activity coefficient on the molal scale. The first term on the right of eq 4 has been found to remain unaltered by a change in molal ratio of chloride to *p*-phenolsulfonate, at constant ionic strength. Under these conditions, then, the change in activity coefficient of hydrochloric acid is described completely by the change in β . Furthermore, this situation may be assumed to persist in the limit of pure buffer, that is, when a negligible concentration of sodium chloride remains. If the mean activity coefficient of hydrochloric acid in the absence of sodium chloride is f_{\pm}° , and the corresponding limit of β is β° , it follows that

$$\log f_{\pm} = \log f_{\pm}^{\circ} + (\beta - \beta^{\circ})\mu, \quad (5)$$

for any given ionic strength. Within the estimated error of 0.002, β varies linearly with the fractional contribution of chloride ion to the total ionic strength of the mixture, $m_3/2\mu = r$. If, then, $\beta - \beta^{\circ} = \alpha'r$, we have, from eq 5,

$$\log(f_{\pm}/f_{\pm}^{\circ}) = \alpha'r\mu = \alpha m_3, \quad (6)$$

where $\alpha' = 2\alpha$. The "activity deviations", $\log(f_{\pm}/f_{\pm}^{\circ})$, of these mixtures are, therefore, a linear function of the molality of sodium chloride at constant total ionic strength. Equation 6 is similar in form to equations that express the linear variation of the logarithm of the activity coefficient of hydrochloric acid with molality of acid in chloride mixtures of constant ionic strength, as found by Harned [9] and by Güntelberg [10].⁴

For the solutions considered here, r varies between 0.01 and 0.1. At 25° C, α' is found to be 0.106. The activity deviations have been computed from eq 6 for four values of r at four ionic strengths. These deviations are given in table 4.

Since the changing ratio of chloride to *p*-phenolsulfonate in the four series of solutions appears not to effect a corresponding change in a_{\pm} , the pH values of all of these mixtures can be computed from a single equation, derived from the law of mass action:

$$\text{pH} = \text{p}K_2 - \log(m_{\text{HPs}}/m_{\text{Ps}}) - 3A\sqrt{\mu}/(1 + 8B\sqrt{\mu}). \quad (7)$$

It is evident, therefore, that the effect of salt on the pH values of

⁴ The linear variation is a consequence of the principle of specific or abnormal salt effects discussed by Acree [11] and coworkers, or specific ionic interaction, as stated by Brönsted [12]. The original Brönsted formulation split the activity coefficient of an ion in a mixture of two electrolytes in dilute aqueous solution into the product of "interaction coefficients" and "salting-out coefficients." Only first-order interactions were considered, and it was assumed that ions are uniformly influenced by ions of like charge as a result of the strong repulsive forces between them. Scatchard and Prentiss [13] extended Brönsted's treatment to include ionic interactions of higher orders. Their experimental work offers extensive confirmation of the basic postulates of the theory. If higher terms are taken into account, the individual thermodynamic properties need no longer vary linearly with composition, although the departure from linearity is small. Small deviations from the results predicted by the theory may, however, indicate the necessity of considering specific effects between ions of like sign, as Harned [9] has shown.

TABLE 4.—Activity deviations in mixtures of constant total ionic strength at 25° C computed from eq 6

$[f_{\pm}/f_{\pm}^*]$ is the ratio of the mean activity coefficient of hydrochloric acid in a mixture of phenolsulfonate buffer and sodium chloride to the activity coefficient in the pure buffer at the same ionic strength. r is the fractional contribution of chloride ion to the ionic strength. α' is 0.106 at 25° C.]

r	$\log (f_{\pm}/f_{\pm}^*)$	r	$\log (f_{\pm}/f_{\pm}^*)$
$\mu=0.05$		$\mu=0.25$	
0.01	0.0001	0.01	0.0003
.025	.0001	.025	.0007
.05	.0003	.05	.0013
.10	.0005	.10	.0027
$\mu=0.10$		$\mu=0.50$	
0.01	0.0001	0.01	0.0005
.025	.0003	.025	.0013
.05	.0005	.05	.0027
.10	.0011	.10	.0053

these buffers in the range of concentrations studied in this investigation is satisfactorily accounted for solely by the change in ionic strength (and activity coefficients) attendant upon the addition of a third ionized component to the buffer. Abnormal or specific effects of the sodium and chloride ions appear to be absent. The pH of a mixture that contains sodium chloride is, therefore, the same as that of a more concentrated buffer of the same ionic strength and buffer ratio to which no salt has been added. This type of behavior might well be termed the *normal salt effect*. On the other hand, a change of a_i (and of pH) with a change of the ratio of sodium chloride to buffer at constant ionic strength would seem to indicate abnormal or specific interactions among the ions.

Equations of the form of eq 7 can be combined by subtraction to represent the pH of a buffer that contains sodium chloride in terms of the value, pH° , for the same buffer in the absence of sodium chloride. Since the first two terms on the right of eq 7 do not change with addition of salt,⁵ the following expression is obtained:

$$\text{pH} = \text{pH}^\circ - 3A \left[\frac{\sqrt{\mu^\circ + m}}{1 + 8B\sqrt{\mu^\circ + m}} - \frac{\sqrt{\mu^\circ}}{1 + 8B\sqrt{\mu^\circ}} \right] = \text{pH}^\circ - 3A\phi(m), \quad (8)$$

where μ° is the ionic strength of the buffer without sodium chloride, m is the molality of sodium chloride, and $\phi(m)$ represents that part of eq 8 inclosed in brackets.

The quantity $\phi(m)$ was evaluated for six buffer solutions in which the molalities of *p*-phenolsulfonate and *p*-phenolate-sulfonate ions were both 0.01, 0.02, 0.04, 0.05, 0.075, and 0.1. Plots of $\phi(m)$ with respect to m suggested that $\phi(m)$ could be represented satisfactorily by $am + bm^2$. The numerical values of a and b were then obtained by the method of least squares and are given in table 5. The following equation permits a calculation of the pH values of these six buffers from 0° to 60° C with a mean deviation of less than 0.001 unit when the

⁵ The salt effect on the hydrolysis of the Ps^- ion is so small at all temperatures from 0° to 60° C that the second term on the right of eq 7 is altered by less than 0.001 pH unit by the addition of 0.1 mole of sodium chloride to a liter of any buffer more concentrated than 0.01 m .

molality of sodium chloride, m , is equal to, or less than, the molality of the buffer:

$$\text{pH} = \text{pH}^\circ - 3A(am + bm^2). \quad (9)$$

The values of $3A$ are given in table 2, and pH° is found in table 6. The change of pH of the six buffer solutions at 25°C with concentration of sodium chloride is shown in figure 2.⁶

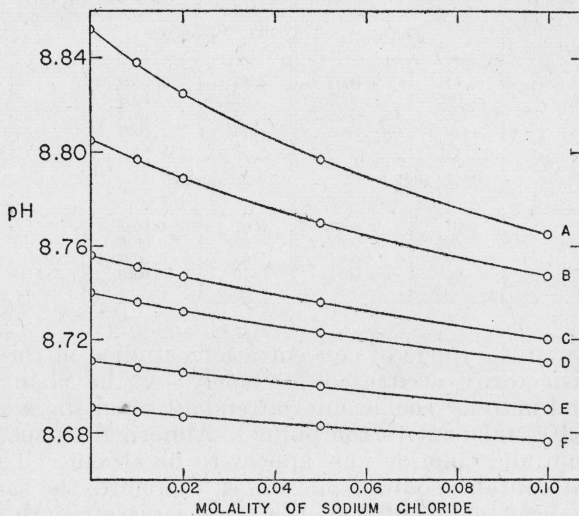


FIGURE 2.—Effect of sodium chloride on the pH values of six phenolsulfonate buffers at 25°C .

Curves A, B, C, D, E, and F represent 0.01, 0.02, 0.04, 0.05, 0.075, and 0.1 molal buffers, respectively.

TABLE 5.—Constants of equation 9

Molality of buffer	a	$-b$	Molality of buffer	a	$-b$
0.01	0.961	4.00	0.05	0.243	0.53
.02	.554	1.75	.075	.167	.38
.04	.306	0.78	.1	.100	.00

IV. STANDARD BUFFER SOLUTIONS

The pH values, pH° , of potassium *p*-phenolsulfonate solutions in which the phenol group is half neutralized with sodium hydroxide and which contain no sodium chloride are listed in table 6 for 13 temperatures from 0° to 60°C . These values were calculated by eq 7 with the use of the second dissociation constant of *p*-phenolsulfonic acid as determined earlier by Bates, Siegel, and Acree [1] and confirmed by the measurements reported in this paper. The compositions of the six buffer solutions are given in table 7. The approximate specific gravities required for the computation of the total volumes of the solutions were estimated from the values for solutions of potassium sulfate and of potassium tartrate. The change of pH with temperature for four of these buffers without sodium chloride is shown in figure 3.

⁶ There is no justification from these experiments for the use of eq 7 and 9 for the calculation of the pH of a buffer-chloride mixture in which the molality of sodium chloride exceeds that of the buffer. It is likely, however, that the linear relationship of eq 6 is valid at somewhat higher values of r than those actually used. These equations have accordingly been employed to compute the pH for molalities of sodium chloride up to one-tenth, as shown in figure 2.

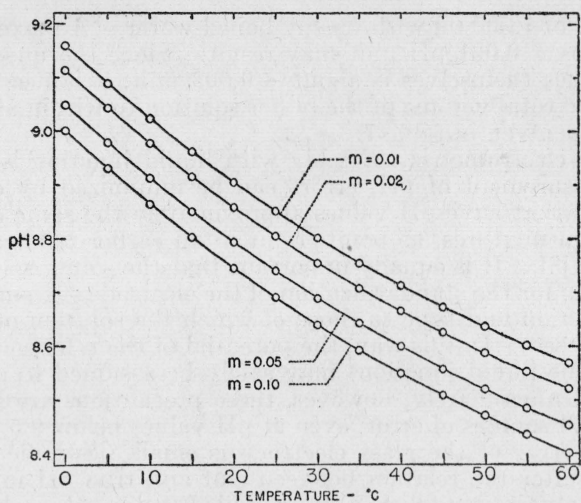


FIGURE 3.—pH of four phenolsulfonate buffers plotted as a function of temperature. The buffer ratio is unity in each case, and m is the molality of potassium *p*-phenolsulfonate and of potassium sodium *p*-phenolate sulfonate.

TABLE 6.—pH values of six phenolsulfonate buffers without sodium chloride from 0° to 60° C

t °C	pH° for—					
	0.01 <i>m</i> buffer	0.02 <i>m</i> buffer	0.04 <i>m</i> buffer	0.05 <i>m</i> buffer	0.075 <i>m</i> buffer	0.1 <i>m</i> buffer
0	9.159	9.113	9.064	9.049	9.021	9.001
5	9.089	9.044	8.995	8.979	8.951	8.931
10	9.024	8.978	8.929	8.913	8.885	8.865
15	8.962	8.916	8.867	8.851	8.823	8.803
20	8.905	8.859	8.810	8.794	8.765	8.745
25	8.852	8.805	8.756	8.740	8.711	8.691
30	8.802	8.755	8.705	8.689	8.660	8.640
35	8.755	8.708	8.659	8.643	8.613	8.593
40	8.713	8.666	8.616	8.600	8.570	8.550
45	8.673	8.626	8.575	8.558	8.529	8.509
50	8.637	8.588	8.538	8.521	8.492	8.472
55	8.601	8.553	8.502	8.485	8.455	8.436
60	8.569	8.521	8.470	8.453	8.423	8.402

TABLE 7.—Compositions of six buffer standards of potassium *p*-phenolsulfonate and sodium hydroxide

Molality of buffer	Potassium <i>p</i> - phenolsulfonate	Sodium hydroxide	Total volume of solu- tion
0.01	4.245	0.01	1,002
.02	8.490	.02	1,005
.04	16.980	.04	1,008
.05	21.23	.05	1,010
.075	31.84	.075	1,012
.1	42.45	.1	1,015

These buffers can be prepared conveniently by dissolving the specified weights of pure potassium *p*-phenolsulfonate in the proper volume of a carbonate-free solution of sodium hydroxide and diluting

to a volume of 1,000 ml with freshly boiled water. A maximum error of slightly over 0.001 pH unit may result. Since the uncertainty in the pH values themselves is about ± 0.003 unit, it is necessary only to adjust the total volume of the buffer solution to within about 20 ml of the figures given in table 7.

When an electrometric assembly with liquid junction is employed for the measurement of pH, errors can be minimized by calibration with buffers that have pH values approximately the same as those of the unknown mixtures, as pointed out in an earlier publication from this Bureau [3]. It is equally important that the solute species in the buffer chosen for the standardization of the electrode system be similar in concentration and type to those of which the solution of unknown pH is composed. In this way, the potential of the reference electrode (including the liquid junction) may safely be assumed to remain unchanged. Unfortunately, however, these precautions are insufficient to remove all sources of error, even at pH values below 9.5, where the sodium-ion error of the glass electrode is small. Specific properties of the ions alter the relation between emf and true pH in a manner that can only be established by detailed study of each solution. Measurements made in this way will accordingly be subject to residual uncertainties of 0.01 to 0.05 pH unit.

It is suggested that *p*-phenolsulfonate buffers be used as standards for the calibration of pH equipment to be used in the range pH 8.0 to 9.0. Phosphate buffers that have a pH of about 7.0 [6] can be used for unknowns up to pH 8.0, and borax solutions (pH about 9.2 [3, 14]) can be employed successfully in the upper range of the phenol-sulfonate buffers and above. When the approximate total ion concentration of the unknown solution can be estimated, the accuracy of the pH measurement can be increased somewhat by use of a standard buffer of approximately the same ionic strength.

V. ESTIMATION OF THE IONIC STRENGTH AND pH OF UNKNOWN MIXTURES OF POTASSIUM *p*-PHENOLSULFONATE AND SODIUM HYDROXIDE

With the use of eq 9 and the constants *a* and *b* given in table 5 it can be shown that the pH of the 0.01 *m* buffer is altered about six times as much as that of the 0.1 *m* buffer upon the addition of a given molal increment of sodium chloride. This dependence of the salt effect on the ionic strength of the buffer suggests the possibility of estimating the ionic strengths and pH values of mixtures of potassium *p*-phenolsulfonate and sodium hydroxide of unknown composition from the change of emf which results from the addition of sodium chloride.

If sodium chloride is added to two portions of the unknown buffer in such amounts that the molality of this salt in solution 1 is m_{C1} and that in solution 2 is $m_{C1} + \Delta m$, and these two solutions are made the electrolytes of cells which contain hydrogen and silver chloride electrodes, the pH values of the solutions are given by

$$pH_1 = (E_1 - E^\circ)/k + \log m_{C1} - A\sqrt{\mu_1}/(1 + 8B\sqrt{\mu_1}) + \beta\mu_1, \quad (10)$$

and

$$pH_2 = (E_2 - E^\circ)/k + \log (m_{C1} + \Delta m) - A\sqrt{\mu_1 + \Delta\mu}/(1 + 8B\sqrt{\mu_1 + \Delta\mu}) + \beta(\mu_1 + \Delta\mu). \quad (11)$$

Subtraction of eq 11 from eq 10 gives an expression for the difference of pH:

$$\text{pH}_1 - \text{pH}_2 = (E_1 - E_2)/k + \log \frac{m_{\text{Cl}}}{m_{\text{Cl}} + \Delta m} + A \left[\frac{\sqrt{\mu_1 + \Delta m}}{1 + 8B\sqrt{\mu_1 + \Delta m}} - \frac{\sqrt{\mu_1}}{1 + 8B\sqrt{\mu_1}} \right] - \beta \Delta m. \quad (12)$$

Furthermore, the pH of each solution can be expressed by eq 7, and the pH difference becomes

$$\text{pH}_1 - \text{pH}_2 = 3A \left[\frac{\sqrt{\mu_1 + \Delta m}}{1 + 8B\sqrt{\mu_1 + \Delta m}} - \frac{\sqrt{\mu_1}}{1 + 8B\sqrt{\mu_1}} \right], \quad (13)$$

since the salt effect on the buffer ratio is negligible (see footnote 5).

Equating the right-hand members of eq 12 and 13 yields an expression for the difference between the emf of the two cells:

$$\begin{aligned} (E_1 - E_2)/k &= 2A \left[\frac{\sqrt{\mu_1 + \Delta m}}{1 + 8B\sqrt{\mu_1 + \Delta m}} - \frac{\sqrt{\mu_1}}{1 + 8B\sqrt{\mu_1}} \right] + \beta \Delta m - \log \frac{m_{\text{Cl}}}{m_{\text{Cl}} + \Delta m} \\ &= 2A\phi(\Delta m) + \beta \Delta m - \log \frac{m_{\text{Cl}}}{m_{\text{Cl}} + \Delta m}, \end{aligned} \quad (14)$$

where $\phi(\Delta m)$ represents the quantity in brackets in eq 12, 13, and 14.

The difference between the emf of the two cells which contain the same buffer but different amounts of sodium chloride can be computed from eq 14 for values of μ_1 , the ionic strength of the more dilute solution, between 0 and 0.5, the probable limits of validity of the equations for pH. When the approximate value of μ_1 has been ascertained, the approximate pH of the solution more dilute in chloride can be computed. For simplicity, eq 10 can be rewritten

$$\text{pH}_1 = (E_1 - E^\circ)/k + \phi(\mu_1), \quad (15)$$

where

$$\phi(\mu_1) = \log m_{\text{Cl}} - \frac{A\sqrt{\mu_1}}{1 + 8B\sqrt{\mu_1}} + \beta \mu_1. \quad (16)$$

The "total salt error," the error in pH which results from considering all activity coefficients equal to unity, is thus $\phi(\mu_1) - \log m_{\text{Cl}}$. A mean value of -0.06 can be employed for β at 25°C . Changes of buffer ratio and ratio of sodium chloride to buffer do not alter the value of a_i and are without marked influence upon β , as may be seen in table 2 of this paper and table 3 of the paper by Bates, Siegel, and Acree [1].

With the use of eq 14 and 16, calculations of $E_1 - E_2$ and $\phi(\mu_1)$ at 25°C have been made for values of μ_1 from 0.02 to 0.50 when $m_{\text{Cl}} = 0.01$, $\Delta m = 0.09$, and $\beta = -0.06$. The results are given in table 8. The conditions for the use of table 8 are met when the molalities of sodium chloride in solutions 1 and 2 are 0.01 and 0.1. The ionic strength of the original mixture is, then, $\mu_1 = 0.01$. The weights of sodium chloride which correspond to these molalities are, respectively, 0.5845 g and 5.845 g for each 1,000 g of solvent. Chloride ion must obviously be absent from the original buffer mixture or, if present

to the extent of not more than 0.01 mole per liter, its concentration determined and the necessary corrections applied to the quantity of salt added.

TABLE 8.—Values of $E_1 - E_2$ and $\phi(\mu_1)$ at 25° C computed from eq 14 and 16 for various values of μ_1

[$m_{Cl} = 0.01$; $\Delta m = 0.09$; $\beta = -0.06$]

μ_1	$E_1 - E_2$	$\phi(\mu_1)$	μ_1	$E_1 - E_2$	$\phi(\mu_1)$	μ_1	$E_1 - E_2$	$\phi(\mu_1)$
0.02	<i>mp</i> 63.28	-2.047	0.22	<i>mp</i> 59.79	-2.113	0.42	<i>mp</i> 59.38	-2.140
.04	62.10	-2.062	.24	59.67	-2.116	.44	59.32	-2.142
.06	61.45	-2.073	.26	59.67	-2.120	.46	59.32	-2.145
.08	60.97	-2.081	.28	59.61	-2.123	.48	59.26	-2.147
.10	60.74	-2.087	.30	59.55	-2.125	.50	59.26	-2.149
.12	60.44	-2.092	.32	59.49	-2.128			
.14	60.26	-2.097	.34	59.44	-2.130			
.16	60.09	-2.102	.36	59.44	-2.133			
.18	59.97	-2.106	.38	59.38	-2.136			
.20	59.85	-2.110	.40	59.38	-2.138			

* The hydrogen-pressure correction to E_1 has been made by the addition of 0.007 to each of the values of $\phi(\mu_1)$ computed from eq 16.

The "total salt error" for each solution of ionic strength μ_1 is given by $\phi(\mu_1) + 2$ (see eq 16).

In eq 10 and 11, E represents the emf of the cell corrected as usual to a partial pressure of hydrogen of 760 mm. The normal barometric pressure in many laboratories is in the vicinity of 760 mm, and the correction to the emf therefore corresponds, for dilute solutions, to an increase of 0.007 unit in pH at 25° C. The values of $\phi(\mu_1)$ listed in table 8 include this correction to the pH, and it is intended that the value of E_1 used in eq 15 shall be the uncorrected emf. An error of not more than 0.006 in pH will result if the barometric pressure is between 740 and 780 mm. A pressure correction is, of course, unnecessary to obtain the difference of emf, $E_1 - E_2$, if the two cells are measured at the same barometric pressure.

When it is desired to obtain by this method the approximate pH of a solution containing unknown quantities of potassium *p*-phenol-sulfonate and sodium hydroxide, sodium chloride is added to two portions of the buffer in amounts which correspond to 0.01 and 0.1 mole per liter of buffer. The potentials between hydrogen and silver chloride electrodes in cells which contain the two buffer-chloride mixtures are measured at 25° C. The difference of emf is obtained and $\phi(\mu_1)$ found from table 8. The pH of the more dilute chloride solution (solution 1) is then computed from eq 15. The values of E° and k are, respectively, 0.2224 and 0.05914. The pH of the original buffer is slightly higher than that of solution 1, but the difference is less than 0.014 unit if the buffer concentration is greater than 0.01.

The substitution of molarity of chloride ion for molality, if necessary, need cause little concern, if an estimate of the ionic strength alone is desired. In order that the last term of eq 14 shall remain equal to 1, it is necessary only to add 0.01 mole and 0.1 mole of sodium chloride to equal volumes of the buffer solution. If this procedure is followed, Δm is no longer exactly 0.09. Changes that amount to less than 5 percent of Δm , however, do not appreciably alter the emf differences listed in table 8. On the other hand, the pH of solution 1 computed from eq 10 may be too low by more than 0.01 unit, if the concentration of chloride ion on the molar scale is used instead of the molality. When 0.01 mole of sodium chloride is added to a liter of

0.1 *m* phenolsulfonate buffer, the concentration of chloride on the molar scale is from 4 to 5 percent lower than the molality, and an error of about 0.02 pH unit will result. As the buffer concentration is lowered, the difference between the concentrations of chloride ion on the weight and volume scales, and consequently the error in pH, will be reduced.

Only a rough estimate of the ionic strength is obtainable by the method outlined here, for the differences of emf, as shown in table 8, are insensitive to small changes of ionic strength when the buffer concentration is high. Fortunately, the corresponding changes of $\phi(\mu_1)$ and of pH are small in this region, and an accurate estimate of ionic strength is unnecessary for the calculation of pH at high concentrations by eq 15. The table also shows, however, that the pH value computed from eq 10 and 15 could be in error by 0.1 unit or more, if the contribution of the buffer to the total ionic strength were ignored completely. The "total salt error" must be carefully considered in dealing with unknowns. Tables similar to table 8 can be constructed for other buffer systems when the values of α_i and β are available. This procedure should find application whenever it is desired to ascertain the approximate ionic strengths of buffer mixtures which vary in concentration but not in type.

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